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Structural and Electrical Characterization of Isotactic PMMA Thin Films Deposited by Spin Coating

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Summary: Thin PMMA films have been studied extensively for their potential applications as membranes, microlithography and optical applications. PMMA has been recently use like gate dielectric film in OTFT. In this paper we present the structural and electrical characteristics of isotactic PMMA (i-PMMA) thin films prepared by spin coating depositions. The electrical characterization was done using a simple capacitive structure to observe current density across dielectric film and voltage breakdown. The i-PMMA films possess low current density across dielectric (1×10^{-8} A/cm^2) and the breakdown voltage is higher than 100 V.

Keywords: FTIR; PMMA; RAMAN; spin coating

Introduction

The poly-methyl-metacrylate (PMMA) is commonly used as resist films in microfabrication processes. Recently this polymer has been of great interest for their potential applications as material for microlithography, optical applications and like dielectric layer in organic thin films transistors (OTFTs)[1,2]. The OTFT have attracted attentions due to their advantages over inorganic thin films transistors in terms of mechanical flexibility, light weight, and low-cost process. The PMMA is a polymer used as a gate dielectric which processes many desirable properties, such as high transmittance, chemical resistance, resistance to weathering corrosion and good insulating properties. In this work we focus on the structural and electrical characteristics of i-PMMA films deposited by spin coating in order to know its properties as dielectric film.

Experimental Part

Isotactic PMMA (i-PMMA) was provided by Aldrich (<80% isotactic). The i-PMMA at 6% was dissolved in anisole and then solution dispersion was promoted by ultrasonic bath for 6 hrs. i-PMMA films were prepared by spin coating on silicon substrate, one sample (i PMMA) was prepared by a drop of solution, to observe the structural characteristics of i-PMMA with-

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out effects of spin deposition. The thickness of all the samples after thermal treatment were around 290 nm. The refractive index obtained was 1.49. These values were obtained by means of variable angle elipsometric measurement, L117 elipsometer. All layers were annealed in three different conditions: at 60°, 90 °C by 20 min and 60 °C by 60 min. The annealing was done to observe the temperature effect on polymer since these films normally are baked in process to fabricate electronic devices [1].

The thickness of each layer was controlled by varying speed during the spin coating process. Film thicknesses were obtained by a reflection/transmission spectrophotometric technique in a Film Tek 3000 system.

Table 1 indicates the deposition condition of the films and the annealing conditions. The thermal annealing was done in order to observe differences in the structure of the sample.

i-PMMA thin films were characterized by micro-RAMAN spectroscopy with 20 mW Ar laser (488 nm) and by Fourier transform infrared spectroscopy, attenuated total reflection (FTIR-ATR) PerkinElmer Spectrum GX with accessory of ATR, in the range between 650 and 4000 cm^{-1}.

The electric characterization was done with a capacitor in order to perform an electrical study before to fabricate a more complex device and in this way to observe the current density across dielectric and the breakdown voltage.

Thin film capacitors were fabricated using a metal-insulator-metal approach i-PMMA as a dielectric film and gold electrodes. After spin deposition of i.-PMMA a thermal treatment at 90 °C by 20 min was realized since these films normally are baked in process to fabricate electronic devices. We fabricate capacitors with different areas at the range of.6×10^{-5} a 2.9×10^{-3} cm^2.

Results and Discussion

Raman Analysis

The RAMAN signal is very sensitive to micro-structural state, provided information on the structure of material on the scale of a few lattice constants. The frequency of phonon RAMAN band depends on the masses and positions of the atoms, the interatomic forces and bond length. Therefore, any effects altering these features will produce changes in the band frequency.

Figure 1 shows the RAMAN spectrum of film deposited without effects of spin (i PMMA) in order to observe its natural structure and compare with film deposited by spin coating. We can observe absorptions bands in the range of 3100-2800 cm^{-1} identified as C–H vibrations of CH_2 y CH_3. The peak associated whit C=O stretching appears around 1720; C–H bending in 1460; C–O stretching in the range of 1270-990 and CH_3 rocking in 816.[3]

Comparison of film i PMMA with the films deposited by spin coating, with different thermal annealing shows in the Figure 2. PMMA films iP6020 and iP9020 deposited by spin coating (Figure 2,c,d) showing very low intensity at PMMA bands and we can observe a mayor intensity in the band related to silicon of substrate around 970 cm^{-1}. The low intensity of the other bands is related to

Table 1.
Deposition condition of the films

Sample	RPM	Thermal Annealing			
		Without thermal annealing	60 °C 20 min	90 °C 20 min	60 °C 60 min
i PMMA	0	ξ			
iP6020	5000		ξ		
iP6060	5000				ξ
iP9020	5000			ξ	

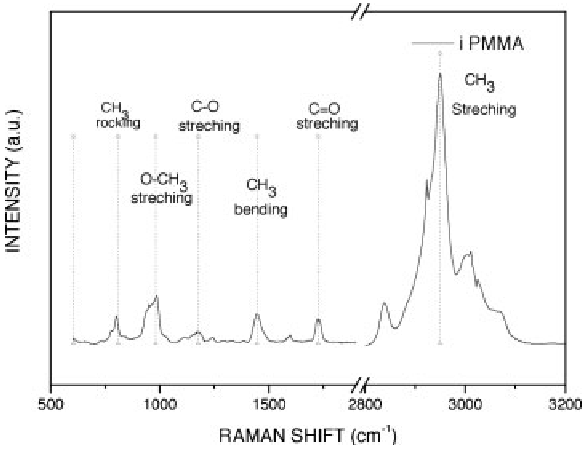

Figure 1.
Raman spectra of a-PMMA film deposited without effects of spin.

the small thicknesses of the films, but in Figure 7.b, in spite of having a 94 nm of thickness, the intensities are mayor, these owes to thermal treatment increase of the films starts order effect in the chains.

FTIR Analysis

FTIR spectra of PMMA are show in Figure 3. The characteristic absorption at 1725 cm^{-1} corresponds to C=O stretching vibration; doubles bands at 1140, 1190 cm^{-1} and 1240, 1265 cm^{-1} correspond to the C−O stretching vibrations of ester groups, peaks at 1440 and 1480 cm^{-1} corresponds to ($C-CH_3$) and ($C-CH_2$) asymmetric bending vibrations bonds.[4] The band related to peaks at 810 and 750 comes from CH_2 rocking vibrations,[5] the bands in the range

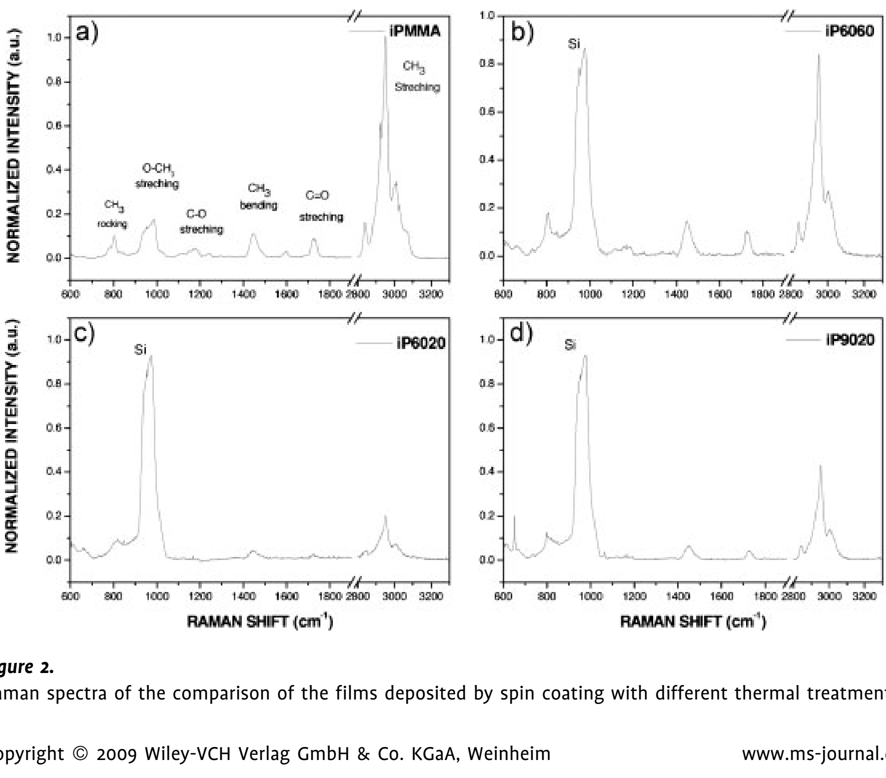

Figure 2.
Raman spectra of the comparison of the films deposited by spin coating with different thermal treatments.

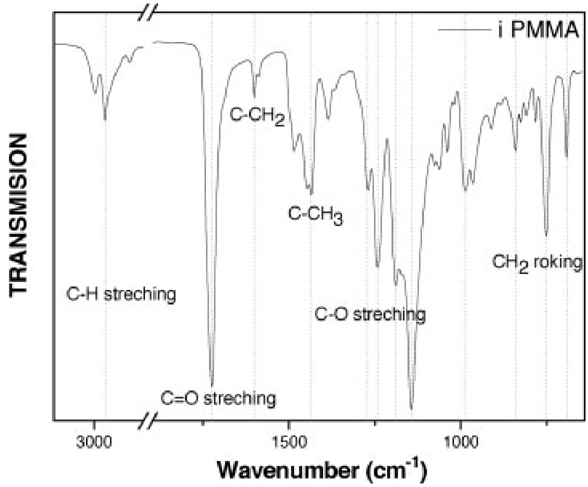

Figure 3.
FTIR spectra of i PMMA.

2850–2998 cm^{-1} are assigned to asymmetric stretching of the C–H bonds.[6]

The Figure 4 shows FTIR spectra of i-PMMA films whit different thermal treatment, the sample iP9020 and iP6060. We can observe that the samples with thermal treatment have a mayor intensity in the bands related to C–H stretching and C=O stretching. This phenomenon can be attributed to a chain breaking and due to oxidation reactions. Oxidation cause the formation of dipoles and trapped charges [4], leading increase IR band intensity of groups such as C=O.

Electrical Characteristics

Thin film capacitors were build using Metal-insulator-metal that uses PMMA as dielectric film and gold electrodes. J-V

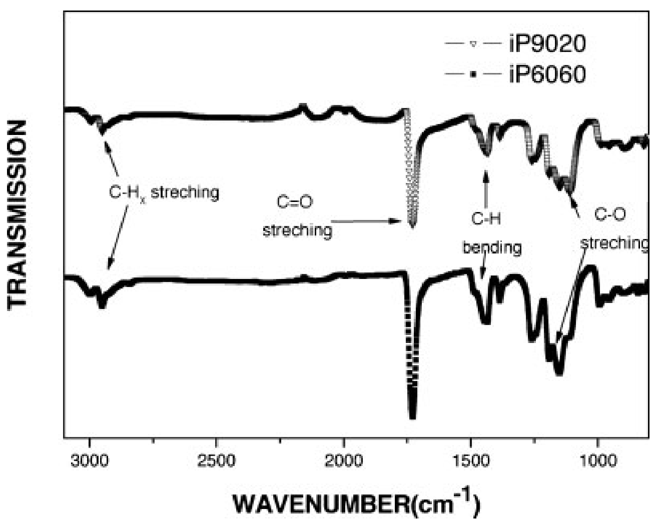

Figure 4.
FTIR spectra of films of PMMA with different thermal treatment, IP9020 (thermal treatment at 90 °C by 20 min) and iP6060 (thermal treatment at 60 °C by 60 min).

measurement was done to observe the current density across of dielectric film. Figure 5 shows current density of three capacitors with the same electrodes area (8.1×10^{-5} cm^2). The current density level of i-PMMA films is below 1×10^{-8} A/cm^2.

The electric field created across the capacitor it's a function of the voltage applied to the electrodes and their separation. At excessively high electric field values, the dielectric material becomes conductive, resulting in a current flow through the capacitor and eventual failure. The applied voltage value where the capacitor begins to conduct is usually referred to as the breakdown voltage. Figure 6 shows the breakdown voltage of some capacitors with an area of 8.1×10^{-5} cm^2, we can observe that the breakdown voltage is mayor than 100 V.

The dielectric constant it was $k_i = 2.6$ and was obtained from C–V measurement

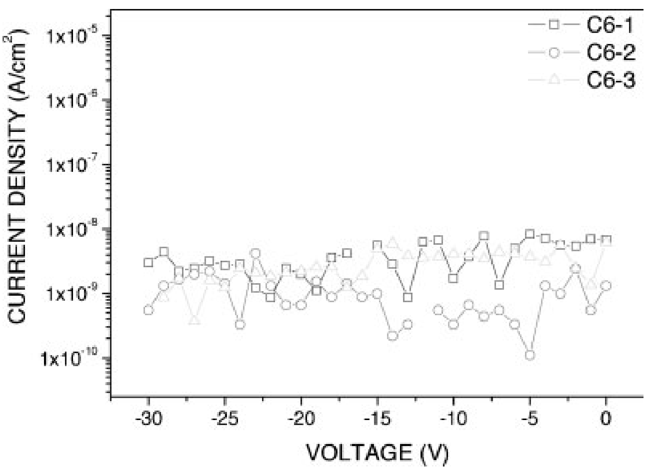

Figure 5.
J-V measurement of capacitors with area of 8.1×10^{-5} cm^2.

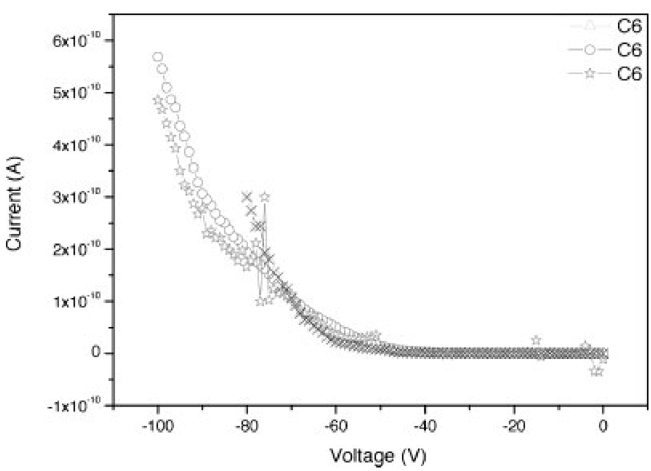

Figure 6.
Breakdown voltage of capacitors with area of 8.1×10^{-5} cm^2.

at 1 MHz through equation (1) which give us the maximum relative capacitance:

$$C_{\max} = \frac{\varepsilon_0 K_i}{x_0} \quad (1)$$

Where:

ε_0 is the permittivity in vacuum.
k_i is the oxide dielectric constant
x_0 is the dielectric thickness

Conclusions

Structural and Electrical characteristics of i-PMMA films were presented. The Raman characterization show an increment in intensity band after thermal treatment related to de effect of order in the chains. FTIR show a light changes in the intensity of bands after thermal annealing due to a chain breaking and due to oxidation reactions. Electrical characteristics was realized in a simple capacitor Au-iPMMA-Au, the current density level of i-PMMA films is low at 1×10^{-8} A/cm^2 and the breakdown voltage was mayor than 100 V. Dielectric constant was obtained from C.V measurement and it was $k_i = 2.6$. These result has to be analyzed in devices like OTFTs.

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